ANALYSIS OF PALLADIUM BY SOLID-LIQUID SEPARATION AFTER LIQUID-LIQUID EXTRACTION. —SPECTROPHOTOMETRIC DETERMINATION OF PALLADIUM(II) BY EXTRACTION OF ITS NIOXIME COMPLEX WITH MOLTEN NAPHTHALENE-

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A procedure is described for the spectrophotometric determination of palladium after extraction of the complex with molten naphthalene. Palladium ion reacts in aqueous solution with complex-forming reagent, nioxime to form a water-insoluble complex in the pH range of 0.5 - 8.5, the complex being easily extracted into molten naphthalene. The extracted mixture of the complex and naphthalene is dissolved in chloroform at 50 °C and the small amounts of palladium are determined spectrophotometrically. The working range of palladium ion concentration and effect of various factors such as pH, amounts of reagent and naphthalene were studied, and the molar absorptivity, sensitivity and relative standard deviation evaluated.

1. Introduction

Spectrophotometric determination of palladium in aqueous solution after extraction of this complex with organic solvent have been widely employed in the analysis of trace amounts of palladium ion. However, the method is not applicable when the solubility of the complex in solvent is small. We have developed a new method " Analysis by solid-liquid separation after liquid-liquid extraction " and have applied it to the determination of palladium with 1,2-cyclohexanedionedioxime (nioxime) as the complexing reagent. Nioxime reacts with palladium(11) to form a water-insoluble complex. This complex is difficult to be extracted into chloroform or benzene, but is easily extracted into molten naphthalene at the temperature above 81°C. After cooling, the mixture of solidified complex and naphthalene is dissolved in chloroform at 50°C and the trace amounts of palladium are determined spectrophotometrically. It is a characteristic of this method that the equilibrium distribution

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in the two phases is attained rapidly and the complex is dissolved merely by contact with molten naphthalene. In the present paper, the extraction of palladium(II) with nioxime into molten naphthalene is reported.

2. Experimental method

2.1 Reagents

Standard palladium solution, 5×10^{-3} M : Prepared by dissolving 0.4433 g of palladium chloride in 20 ml of concentrated hydrochloric acid and diluting to 500 ml with deionized water. More dilute palladium solutions were prepared as required by diluting the standard solution.

Nioxime solution : 0.5 % in ethanol.

Buffer solution : Appropriate mixtures of 1M acetic acid and 1M ammonium acetate or 1M ammonia water and 1M ammonium acetate.

Naphthalene, chloroform and all other reagents were of analytical reagent grade, and were used without further purification.

The water used was deionized water.

2.2 Apparatus

The apparatus used in this experiment are a Hitachi Model 200-20 spectrophotometer with matched 10 mm glass cells and a Toa-Dempa HM-6A pH meter equipped with combined glass and calomel electrodes.

2.3 Procedure

To 25 ml of the sample solution containing 1 - 6 ml of 5×10^{-4} M palladium chloride, in a 80 ml tightly stoppered Erlenmeyer flask, add 1.5 ml of 0.5 % nioxime ethanol solution and 2 ml of acetic acid-ammonium acetate buffer solution, and adjust the pH to about 4.5. Mix the solution well, and warm it on a water bath at around 60 °C. Add 2.0 g of naphthalene and warm the mixture in the water bath at 90 °C to melt naphthalene completely. Shake it vigorously till the naphthalene solidifies, forming many fine crystals and allow to cool to room temperature. Again warm and melt the very fine crystals slowly, and let them grow to give a coarser crystalline deposit. Cool to room temperature, collect the solidified deposit on a filter paper, wash with water, and blot the surplus water with a dry filter paper. Spread the crystals on a filter paper and allow to dry. Then dissolve them with hot chloroform at 50 °C by vigorous shaking and dilute to 10 ml. Dry the solution by addition of about 2 g of anhydrous sodium sulfate, transfer a portion into a 10 mm glass cell and measure its absorbance at 375 nm against a reagent blank prepared similarly. Calculate the amount of

palladium from the calibration curve.

3. Result and discussion

3.1 Absorption spectra

The absorption spectra of nioxime and palladium-nioxime complex in naphthalene-chloroform solution, measured against water, are shown in Fig.1. Absorption curve of palladium complex has two shoulders at 350 and 380 nm. The reagent blank shows strong absorption below 340 nm, but beyond this wavelength, there is practically a negligible absorption due to the reagent blank. Therefore, all the absorbance measurements were performed at 385 nm throughout this experiment.

3.2 Effect of pH on absorbance

The pH value of the solution containing 160 μg of palladium and 1.5 ml of 0.5 % nioxime ethanol solution was carefully controlled to — 11.0 with hydrochloric acid, acetic acid-ammonium acetate or ammonia-ammonium acetate buffer solution. The pH values of the aqueous solution after extraction were measured at room temperature. The relationship between the absorbance and pH of the aqueous solution after extraction was studied, and the results obtained are shown in Fig. 2. From these, it is clear that the extraction starts from 2N hydrochloric acid solution, increases sharply, gives a definite and maximum value in the pH range of 0.5 - 8.0, and again decreases slowly beyond pH 8.0. Therefore, the pH range of 0.5 - 8.0 is suitable for quantitative extraction of palladium.

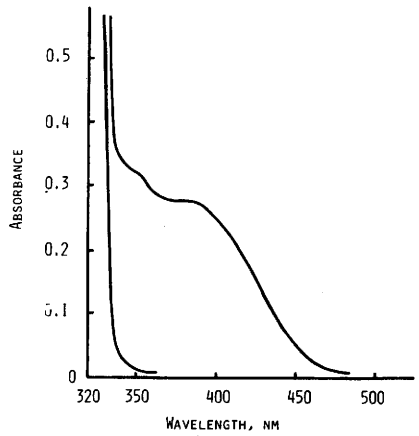

FIG. 1 ABSORPTION SPECTRA OF NIOXIME AND PALLADIUM COMPLEX IN NAPHTHALENE-CHLOROFORM SOLUTION
PALLADIUM : 160 μG ; 0.5 % NIOXIME : 1.5 ML ; pH : 4.5 ;
BUFFER SOLUTION : 2.0 ML ; NAPHTHALENE : 2.0 G ;
DIGESTION TIME : 10 MIN ; STANDING TIME : 10 MIN
REFERENCE : WATER

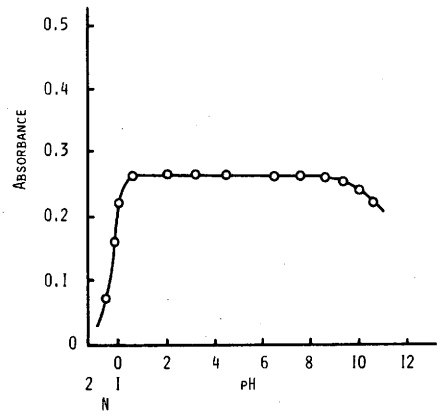

FIG. 2 EFFECT OF pH ON ABSORBANCE
PALLADIUM : 160 μG ; 0.5 % NIOXIME : 1.5 ML ; BUFFER SOLUTION : 2.0 ML ; WAVELENGTH : 375 NM ; NAPHTHALENE 2.0 G ; STANDING TIME : 10 MIN ; SOLVENT : CHLOROFORM
REFERENCE : REAGENT BLANK

3.3 Effect of reagent concentration on absorbance

Various amounts of nioxime were added to the solution containing 160 μg of palladium at pH about 4.5, and the effect of variation in the nioxime concentration on the absorbance of the complex has been studied. The result obtained is shown in Fig. 3. It indicates that 0.1 - 5.0 ml of 0.5 % nioxime solution are quite appropriate for the quantitative extraction of palladium. Therefore, 1.5 ml of 0.5 % nioxime solution were taken throughout this experiment.

3.4 Effect of buffer solution on absorbance

Sample solution containing 160 μg of palladium, 1.5 ml of 0.5 % nioxime solution and various amounts of the acetate buffer solution in total volume of about 30 ml was prepared, and the palladium complex in solution was extracted with 2.0 g of naphthalene. After cooling, the absorbance of mixture of palladium complex and naphthalene in the chloroform solution was measured at 375 nm against the reagent blank. The amounts of the acetate buffer solution(pH 4.5) were varied from 0.5 to 5.0 ml at intervals of 0.5 ml. The result obtained is shown in Fig.4. From this experimental result, the absorbances were almost constant independently of the amounts of the acetate buffer solution. Therefore, 2.0 ml of the acetate buffer solution were added throughout this experiment.

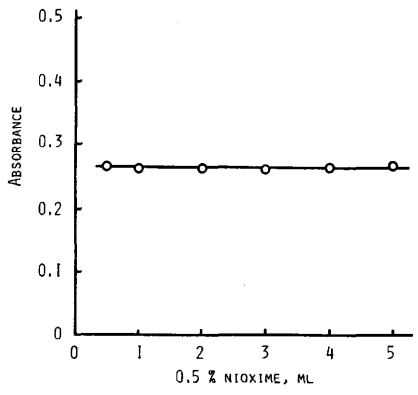

FIG. 3 EFFECT OF REAGENT CONCENTRATION ON ABSORBANCE
PALLADIUM : 160 μG ; 0.5 % NIOXIME : 1.5 ML ; PH : 4.5 ML ; NAPHTHALENE : 2.0 G ; WAVELENGTH : 375 NM ; DIGESTION TIME : 10 MIN ; SOLVENT : CHLOROFORM
REFERENCE : REAGENT BLANK

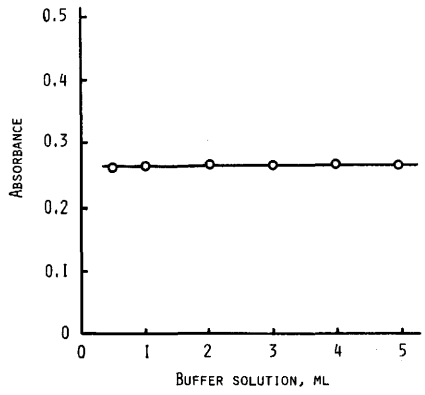

FIG. 4 EFFECT OF BUFFER SOLUTION ON ABSORBANCE
PALLADIUM : 160 μG ; 0.5 % NIOXIME : 1.5 ML ; PH : 4.5 ; WAVELENGTH : 375 NM ; DIGESTION TIME : 10 MIN
REFERENCE : REAGENT BLANK

3.5 Effect of digestion time on absorbance

A mixture containing 160 μg of palladium, 1.5 ml of 0.5 % nioxime solution and 2.0 ml of the acetate buffer solution(pH 4.5) was warmed on the water bath at 60 °C till larger particles of palladium complex were

formed. The effect of digestion time(5 - 50 min) on the absorbance of the complex is shown in Fig. 5. It indicates that the complex is very stable at high temperature and the long digestion times do not give effect on the absorbance. The speed of extraction by shaking is very fast owing to high temperature and only several seconds' shaking was sufficient to extract palladium complex completely.

3.6 Effect of addition of naphthalene on absorbance

The amounts of naphthalene were varied from 0.5 to 3.0 g and the extraction was carried out by the recommended procedure. The result obtained is shown in Fig. 6. The absorbance did not vary by increasing amounts of naphthalene. Large amounts of naphthalene made the experimental operations difficult owing to the sublimation of naphthalene, which was followed by the volatilization of chloroform. The value of chloroform required to dissolve 1 g of naphthalene was 2 ml. Therefore, 2.0 g of naphthalene were used for further study.

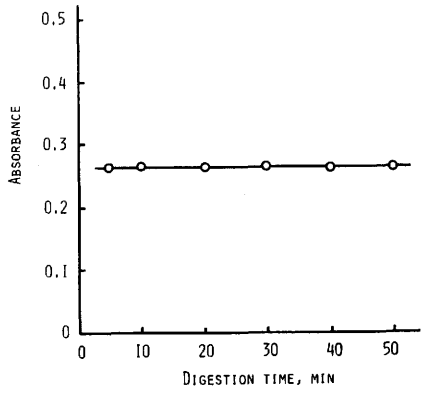

FIG. 5 EFFECT OF DIGESTION TIME ON ABSORBANCE
PALLADIUM : 160 μG ; PH : 4.5 ; 0.5 % NIOXIME : 1.5 ML ;
WAVELENGTH : 375 NM ; BUFFER SOLUTION : 2.0 ML ;
REFERENCE : REAGENT BLANK

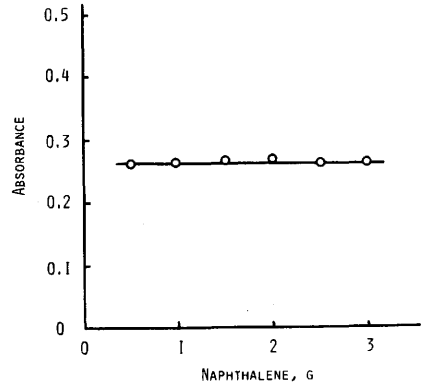

FIG. 6 EFFECT OF AMOUNT OF NAPHTHALENE ON ABSORBANCE
PALLADIUM : 160 μG ; 0.5 % NIOXIME : 1.5 ML ; PH : 4.5 ;
BUFFER SOLUTION : 2.0 ML ; DIGESTION TIME : 10 ML
REFERENCE : REAGENT BLANK

3.7 Effect of standing time on absorbance

Sample solution containing 160 μg of palladium, 1.5 ml of 0.5 % nioxime solution and 2.0 ml of the acetate buffer solution(pH 4.5) in total volume of about 30 ml was prepared according to the recommended procedure, and the extraction was carried out with 2.0 g of naphthalene. The mixture of the complex and naphthalene was dissolved in hot chloroform at 50 °C. After cooling to room temperature, the effect of standing time on the absorbance of chloroform solution was investigated between 10 and 120 min. The result obtained is shown in Fig. 7. The complex in naphthalene-chloroform solution is very stable in both low and high temperature and the change of the color was not almost recognized for a

long time.

3.8 Calibration curve

With the optimum conditions described above, the calibration curve for palladium determination was established at the wavelength of 375 nm against the reagent blank. The result obtained is shown in Fig. 8. It was linear over the range of 28 - 320 μg of palladium(II) in 10 ml of chloroform. The molar absorptivity was calculated to be 1.8×10^3 $l \cdot mol^{-1} \cdot cm^{-1}$, and the sensitivity 0.060 μg of palladium per cm^2 for the absorbance of 0.001. Ten sample solutions containing 160 μg of palladium, prepared by the recommended procedure, gave a mean absorbance of 0.265, with a standard deviation of 0.0015(relative standard deviation of 0.55 %).

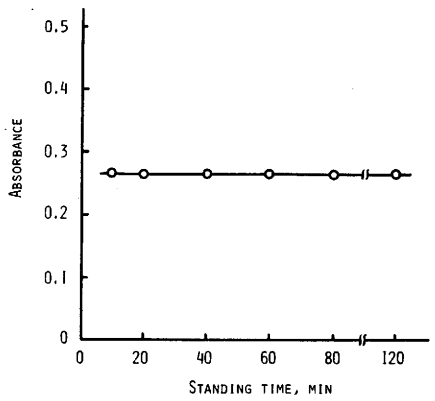

FIG. 7 EFFECT OF STANDING TIME ON ABSORBANCE
PALLADIUM : 160 μG ; 0.5 % NIOXIME : 1.5 ML ; PH : 4.5 ; NAPHTHALENE : 2.0 G ;DIGESTION TIME : 10 MIN ; WAVELENGTH : 375 NM ; STANDING TIME : 10 MIN ; SOLVENT : CHLOROFORM
REFERENCE : REAGENT BLANK

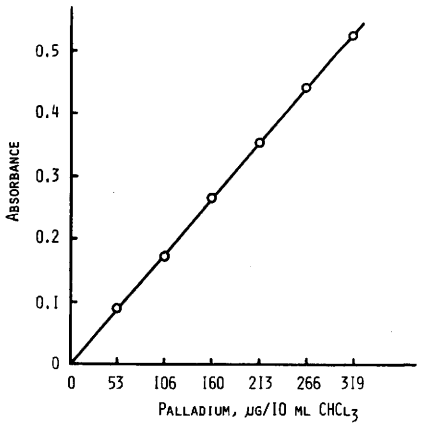

FIG. 8 CALIBRATION CURVE FOR PALLADIUM
WAVELENGTH : 375 NM ; 0.5 % NIOXIME : 1.5 ML ; PH : 4.5 ; BUFFER SOLUTION : 2.0 ML ; NAPHTHALENE : 2.0 G ; DIGESTION TIME : 10 MIN ; STANDING TIME : 10 MIN
REFERENCE : REAGENT BLANK